Chapter 23 - **EMPIRICAL MODELS**

Standard plots give the first order interpretation of SANS data. Precise models give a more detailed approach at obtaining results. Precise molecular models are however not always available or too complex to use. An intermediate approach consists in using empirical models that reproduce the main trends observed in the SANS data. Some of these models are described here.

1. THE CORRELATION LENGTH MODEL

Oftentimes when the scattering intensity I(Q) is a decreasing function with Q, it is modeled using the following functional form:

$$I(Q) = \frac{C}{1+(Q\xi)^m} + B. \qquad (1)$$

Here C and B are (Q-independent) constants obtained for $I(Q\xi \to 0) = C + B$ and $I(Q\xi \to \infty) = B$, ξ is a correlation length and m is a Porod exponent. Note that when m = 2, this functional form becomes the familiar Lorentzian function. The Fourier transform of a Lorentzian function corresponds to correlations dying out as $\exp(-r/\xi)/r$. The correlation length ξ is large for systems that are highly correlated like polymers and gels. For example, ξ is equal to the entanglement distance for a semi-dilute polymer solution and it is equal to the end-to-end distance for very dilute polymers. Note that the low-Q limit of this empirical form reproduces the Guinier law only when m = 2.

A figure shows SANS data from 4 % (g/g) solution of poly(ethylene oxide) or PEO for short of M_w = 41,500 g/mol in D_2O at a temperature of 20 ^{o}C (Hammouda et al, 2004). Fit to the correlation length model gave the following parameters: C = 0.52 cm^{-1}, ξ = 17.47 Å, m = 1.93 and B = 0.069 cm^{-1}. The fit is good except for the very low-Q points where statistics are poor. The correlation length ξ gives a good estimate of the average entanglement length for this semi-dilute polymer solution. The Porod exponent m points to a "mass fractal" for dissolved polymer chains close to the theta condition. The fractal exponent for chains in a good solvent is m = 5/3 and that for chains in theta condition is m = 2. The theta condition is defined when the monomer-solvent, monomer-monomer and solvent-solvent molecular interactions are comparable.

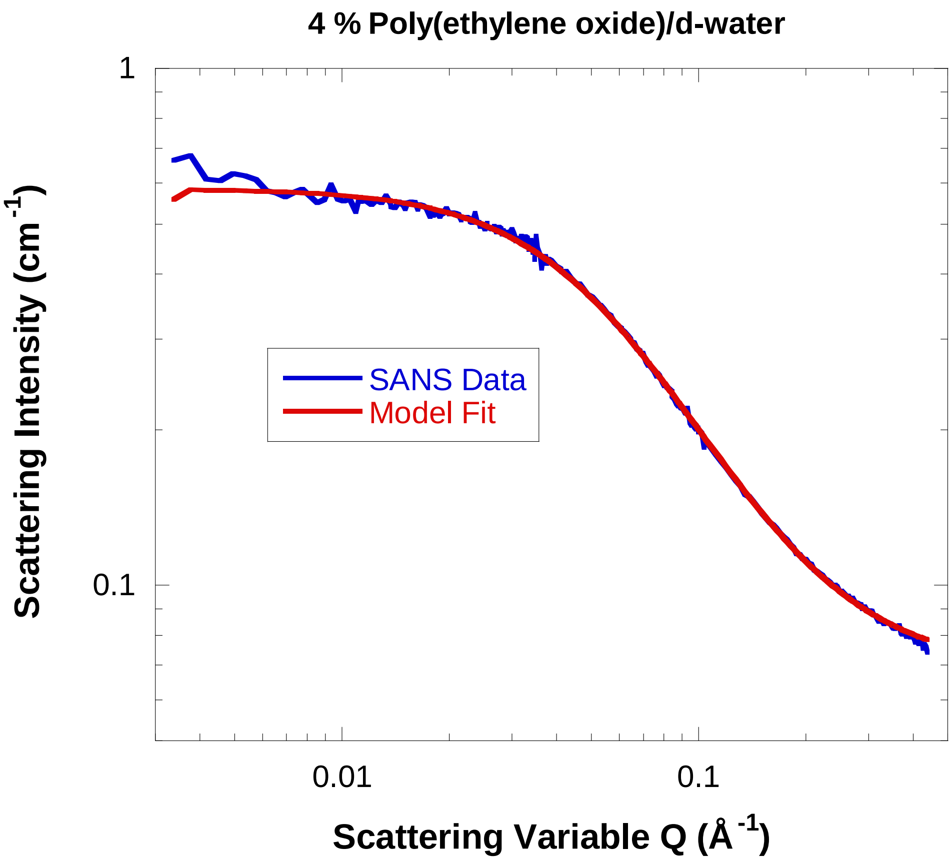

Figure 1: SANS data from 4 % solution of PEO (M_w = 41,500 g/mol) in D_2O at 20 °C temperature and fit to the correlation length model.

2. THE MODIFIED CORRELATION LENGTH MODEL

In some cases where there is a low-Q power law behavior, the correlation length model is model to incorporate a "stretching" feature in the low-Q mass fractal structure.

$$I(Q) = \frac{1}{Q^s}\frac{C}{1+(Q\xi)^m} + B \tag{2}$$

Here also ξ is a characteristic length and m is a high-Q Porod exponent. Parameter s is a "stretching" factor (s = 0 for isotropic structure and s = 1 for fully stretched mass fractal (think network) structure. Note that when m = 2 and s = 0, this functional form becomes the Lorentzien and ξ is the correlation length (1/e-folding length in r-space).

SANS data and fit to the correlation length model are included for a POSS (generation 3) dendrimer in d-THF solution at 100 mg/ml mass fraction and ambient temperature (25 °C). Fit results yielded the following parameters s = 0.68 and ξ = 14.51 (Yuan et al, 2016).

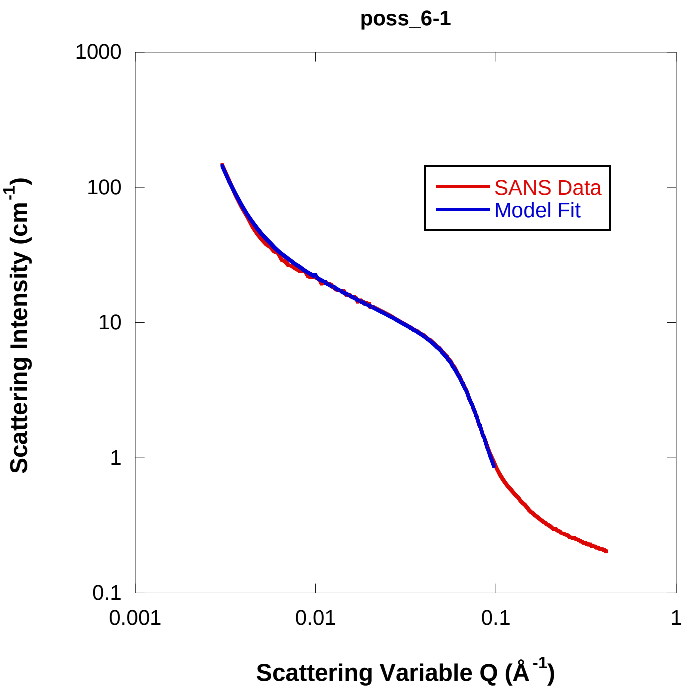

Figure 2: SANS data and fit to the modified correlation length model for a POSS dendrimer ($POSS_{65}$-PEG_{392}) in d-THF at 100 mg/ml mass fraction and ambient temperature (25 ^{o}C).

3. THE BROAD PEAK MODEL

Many SANS spectra are characterized by a broad peak even though they are from amorphous soft materials. The d-spacing corresponding to the broad peak is a characteristic distance between the scattering inhomogeneities (such as in lamellar, cylindrical, or spherical morphologies or for bicontinuous structures). The following simple functional form reproduces the broad peak feature:

$$I(Q) = \frac{C}{1+\left(|Q-Q_0|\xi\right)^m} + B. \tag{3}$$

Here the peak position is related to the d-spacing as $Q_0 = 2\pi/d_0$. Soft systems that show a SANS peak include copolymers, polyelectrolytes, multiphase systems, layered structures, etc.

A figure shows SANS data from 4 % poly(lysine) polyelectrolyte solution in D_2O at 25 ^{o}C temperature. Poly(lysine) is a poly(amino acid). Fit to the broad peak model gave the following parameters: C = 0.075 cm^{-1}, ξ = 13.10 Å, Q_0 = 0.099 Å^{-1}, m = 1.05 and B = 0.064 cm^{-1}. Here again, the fit is good except for the low-Q points where statistics are poor. The d-spacing is $d_0 = 2\pi/Q_0 = 63.47$ Å. This is an average inter-distance between charged polyelectrolyte domains.

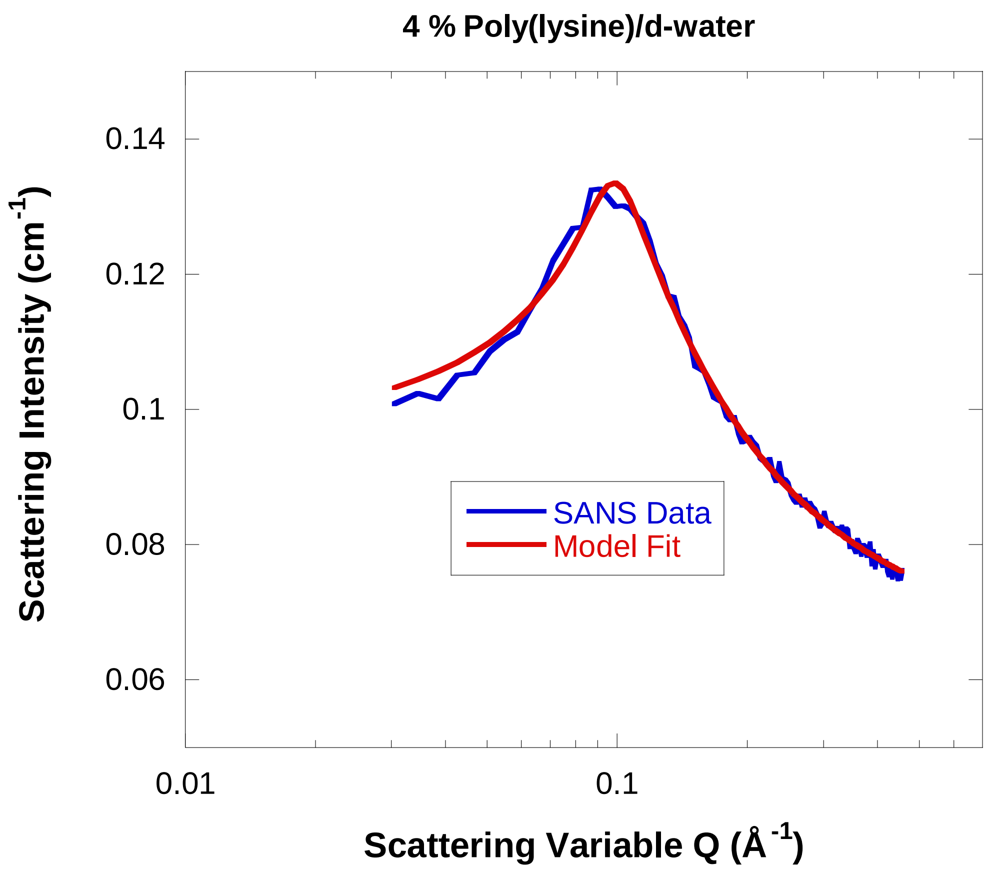

Figure 3: SANS data from 4 % poly(lysine) poly(amino acid) solution in D_2O at 25 ^oC temperature and fit to the broad peak model.

4. THE TEUBNER-STREY MODEL

The Teubner-Strey model (Teubner-Strey, 1987) was originally introduced to represent the structure of micellar systems. These are characterized by a peak representing inter-micellar interactions. This model assumes a pair correlation function of the form:

$$\gamma(r) = \frac{d}{2\pi r} \exp\left(-\frac{r}{\xi}\right) \sin\left(\frac{2\pi r}{d}\right). \qquad (4)$$

Here ξ is a correlation length (length beyond which correlations die out) and d is a d-spacing (characteristic of a domain size or periodicity). Recall that the coherent macroscopic scattering cross section is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \phi\Delta\rho^2 V_P P(Q) S_I(Q) = \phi\Delta\rho^2 \int_0^\infty dr r^2 4\pi \frac{\sin(Qr)}{Qr}\gamma(r) \quad (5)$$

ϕ is the sample volume fraction, V_P is the scattering “particle” volume, $\Delta\rho^2$ is the contrast factor, P(Q) is the form factor and $S_I(Q)$ is the structure factor. Performing this integration yields:

$$\frac{d\Sigma(Q)}{d\Omega} = \phi\Delta\rho^2 \frac{8\pi\xi^3}{\left[1+\left(\frac{2\pi\xi}{d}\right)^2\right]^2 + \left[-2\xi^2\left(\frac{2\pi\xi}{d}\right)^2 + 2\xi^2\right]Q^2 + \xi^4 Q^4}. \quad (6)$$

The functional form for the scattering intensity can therefore be presented in the form:

$$I(Q) = \frac{d\Sigma(Q)}{d\Omega} + B = \phi\Delta\rho^2 \frac{\left(\frac{8\pi}{\xi}\right)}{\left[\frac{a_2}{c_2} + \frac{c_1}{c_2}Q^2 + Q^4\right]} + B. \quad (7)$$

B is a Q-independent incoherent scattering background. The various parameters a_2, c_1 and c_2 are defined as:

$$\frac{a_2}{c_2} = \frac{\left[1+\left(\frac{2\pi\xi}{d}\right)^2\right]^2}{\xi^4} \qquad \frac{c_1}{c_2} = \frac{\left[-2\xi^2\left(\frac{2\pi\xi}{d}\right)^2 + 2\xi^2\right]}{\xi^4}. \quad (8)$$

These are considered as fitting parameters. The correlation length ξ and the d-spacing d can be expressed as:

$$\xi = \frac{1}{\sqrt{\frac{1}{2}\sqrt{\frac{a_2}{c_2}} + \frac{1}{4}\frac{c_1}{c_2}}} \quad (9)$$

$$d = \frac{2\pi}{\sqrt{\frac{1}{2}\sqrt{\frac{a_2}{c_2}} - \frac{1}{4}\frac{c_1}{c_2}}}.$$

A factor $f_a = c_1/\sqrt{4a_2c_2}$ is defined to represent the amphiphile “strength” which dictates the microstructure. For example, the ordered lamellar phase corresponds to $f_a = -1$ while the disordered phase corresponds to $f_a = 1$.

Consider SANS data from 10 % P85 Pluronic (triblock copolymer of PEO-PPO-PEO) measured in D_2O at 60 ^oC (temperature for which the micelles are well formed). Fits of the SANS data to the Teubner-Strey model yields the following fitting results.

$$a_2 = 0.038 \qquad (10)$$
$$c_1 = -51.23$$
$$c_2 = 24{,}929$$
$$B = 0.118.$$

Note that for the functional form to produce a peak, parameter c_1 has to be negative. These parameters give the following value for the two characteristic lengths:

$$\xi = 96 \text{ Å} \qquad (11)$$
$$d = 186.6 \text{ Å}.$$

Adding a constant incoherent level B, the scattering intensity (coherent and incoherent contributions) are $I(Q) = d\Sigma(Q)/d\Omega + B$.

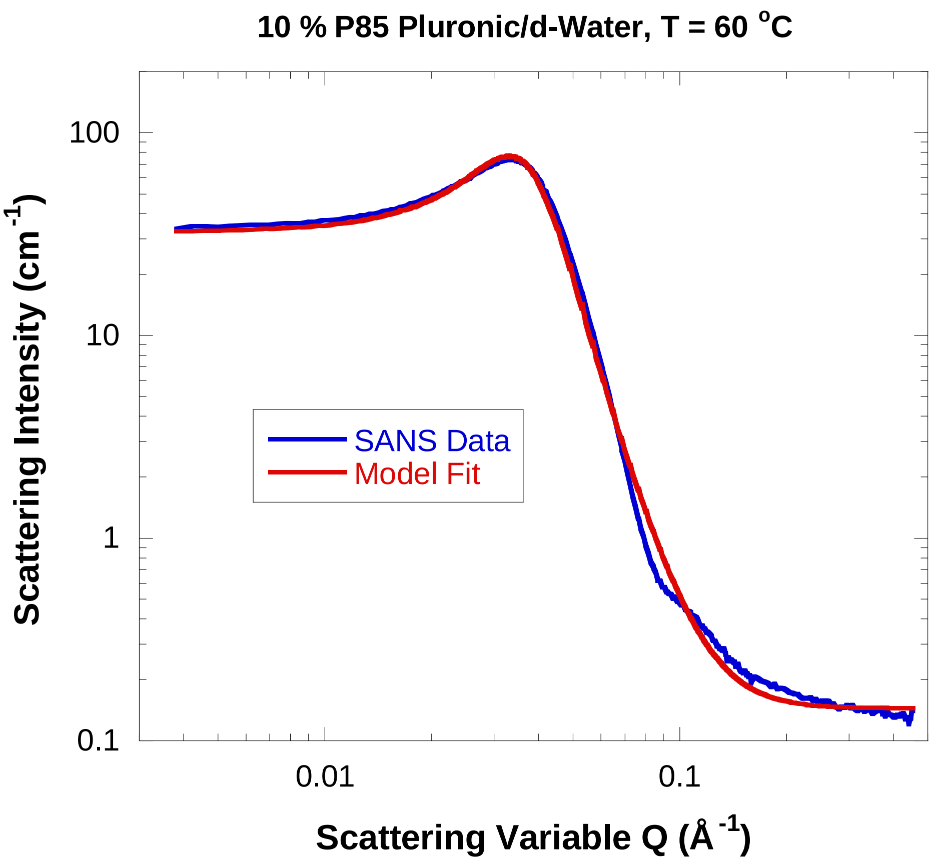

Figure 4: SANS data from 10 % P85 Pluronic in D_2O at 60 ^oC plotted along with the fit to the Teubner-Strey model.

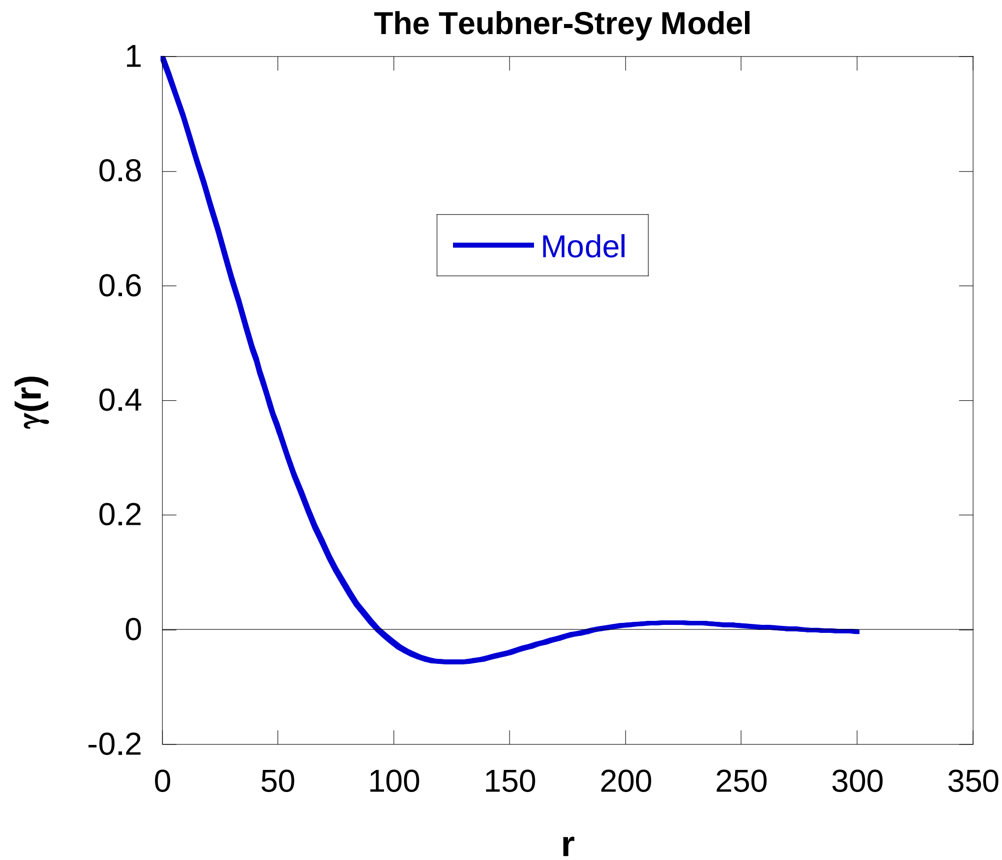

Figure 5: The pair correlation function $\gamma(r)$ for the Teubner-Strey model.

Note that a peaked behavior in I(Q) results in a pair correlation function $\gamma(r)$ going negative then positive. This is referred to as the "correlation hole" effect. This happens in block copolymers, in polyelectrolytes and in concentrated systems.

The Teubner-Strey model applies to concentrated solutions of particles (spheres, cylinders, etc) and to the bicontinuous structure. It does not do well for lamellar systems and for other highly ordered morphologies (for example, ordered diblock copolymers). It misses the higher order oscillations completely. Moreover, the Teubner-Strey model was developed for water/oil/surfactant ternary mixtures in the micelle-formation region. Using it for polymer/copolymer mixtures requires some adjustments.

5. THE DEBYE-BUECHE MODEL

The Debye-Bueche model is used to describe scattering from phase-separated (two-phase) systems. Here also correlations are characterized by an e-folding length ξ. The pair correlation function is give by (Debye-Bueche, 1949):

$$\gamma(r) = \exp\left(-\frac{r}{\xi}\right). \qquad (12)$$

The scattering cross section is obtained by taking the Fourier transform to obtain:

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{C}{\left[1+(Q\xi)^2\right]^2}. \qquad (13)$$

The prefactor can be expressed in terms of the volume fraction ϕ and contrast factor $\Delta\rho^2$ as:

$$C = 8\pi\Delta\rho^2\phi\xi^3. \qquad (14)$$

The Debye-Bueche model is obtained as a special case of the Teubner-Strey model for very large d-spacing (d>>ξ).

6. THE GUINIER-POROD MODEL

An empirical Guinier-Porod model is useful for analyzing SANS data (Hammouda, 2010). The scattering intensity is given by the two contributions:

$$I(Q) = G\exp\left[\frac{-Q^2 R_g{}^2}{3}\right] \text{ for } Q \le Q_1 \qquad (15)$$

$$I(Q) = \frac{D}{Q^m} + B \text{ for } Q \ge Q_1.$$

Note that the incoherent scattering has been added as a constant (Q-independent) term. Imposing that the values of the Guinier and Porod terms and their slopes (derivatives) be continuous at a value Q_1 yields the following relationships:

$$Q_1 = \frac{1}{R_g}\sqrt{\frac{3m}{2}} \qquad (16)$$

$$D = G\exp\left[\frac{-Q_1{}^2 R_g{}^2}{3}\right] Q_1{}^m = G\exp\left[-\frac{m}{2}\right]\left(\frac{3m}{2}\right)^{\frac{m}{2}}\frac{1}{R_g{}^m}.$$

The Guinier form is used for $Q \le Q_1$ and the Porod form is used for $Q \ge Q_1$. Note that the value of Q_1 does not have to be set; it is calculated internally using Eq. 2. This model is general and should apply in the entire range of Porod parameters. It is completely empirical.

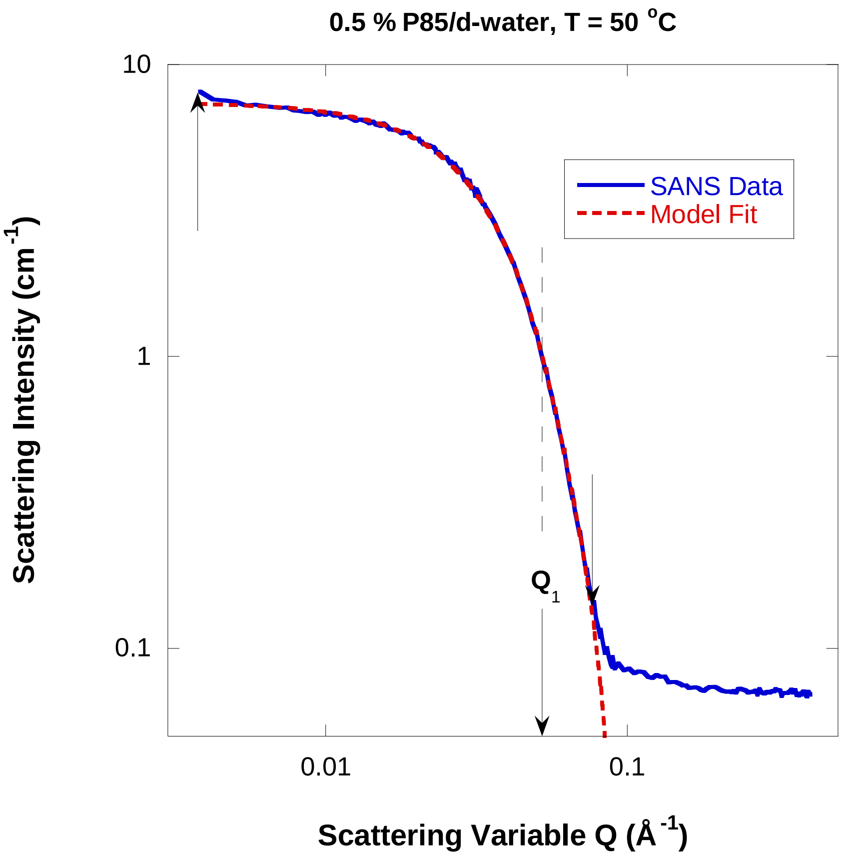

Figure 6: SANS data and fit to the Guinier-Porod model for 0.5% P85/d-water at 50 °C where spherical micelles are formed. Note that the high-Q background has been excluded from the fit. The fitting region is delimited by arrows.

This model is generalized to account for asymmetric scattering objects (such as rods or lamellae) as follows:

$$P(Q) = \frac{G}{Q^s} \exp\left[\frac{-Q^2 R_g^{\ 2}}{3-s}\right] \quad \text{for} \quad Q \le Q_1 \tag{17}$$

$$P(Q) = \frac{D}{Q^m} + B \quad \text{for} \quad Q \ge Q_1 .$$

This is based on the generalized Guinier law for such elongated objects (Glatter-Kratky, 1982). The same scaling factor G has been kept even though it has different units. For 3D globular objects (such as spheres), s = 0 and one recovers the previous results. For 2D symmetry (such as for rods) s = 1 and for 1D symmetry (such as for lamellae or platelets) s = 2. The dimensionality parameter corresponds to 3-s.

Applying the same continuity of the Guinier and Porod functions and their derivatives yields to the generalized Guinier-Porod model yields:

$$Q_1 = \frac{1}{R_g}\sqrt{\frac{(m-s)(3-s)}{2}} \tag{18}$$

$$D = G\exp\left[\frac{-Q_1{}^2 R_g{}^2}{3-s}\right] Q_1{}^{(m-s)} = \frac{G}{R_g{}^{(m-s)}}\exp\left[-\frac{(m-s)}{2}\right]\left(\frac{(m-s)(3-s)}{2}\right)^{\frac{(m-s)}{2}}$$

This empirical model is used to analyze SANS data from a Pluronic P85 which consists of the following block sequence $EO_{26}PO_{40}EO_{26}$ where EO and PO represent ethylene oxide and propylene oxide monomers respectively. A 0.5 % P85/d-water is known to form micelles upon heating. It forms spherical micelles at 50 °C, cylindrical micelles at 70 °C and lamellar micelles at 90 °C.

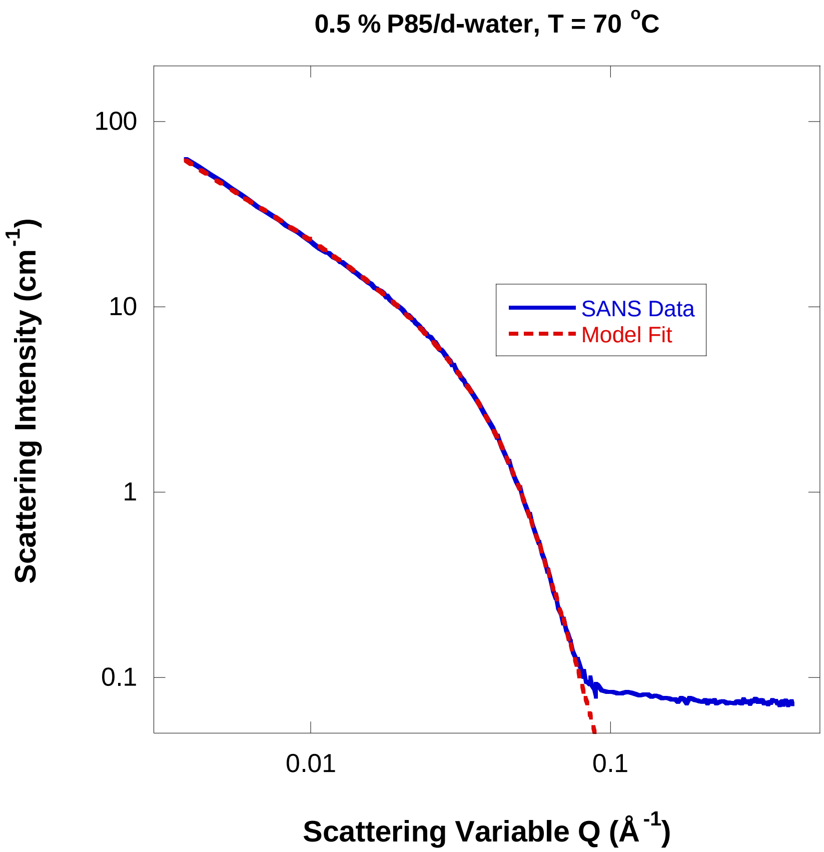

Figure 7: Fit of the generalized Guinier-Porod model to the SANS data from 0.5% P85/d-water at 70 °C where cylindrical micelles are formed.

Nonlinear least squares fit yields the following parameters for the scale factor G, dimensionality parameter 3-s, the radius of gyration Rg and the Porod exponent m.

$$G = 0.32 \tag{19}$$

$3\text{-}s = 2.06$
$R_g = 37.1$ Å
$m = 4.82$.

Note that this single model can fit SANS data from spherical micelles ($s = 0$), cylindrical micelles ($s = 1$) and lamellar micelles ($s = 2$) as well as intermediate structures.

REFERENCES

B. Hammouda, D. Ho and S. Kline, "Insight into Clustering in Poly(ethylene oxide) Solutions", Macromolecules 37, 6932-6937 (2004)

M. Teubner and R. Strey, "Origin of the Scattering Peak in Microemulsions", J. Chem. Phys. 87, 3195-3200 (1987)

O. Glatter, and O. Kratky, "Small-Angle X-Ray Scattering", Academic Press. Check out Chapter 4 on Data Treatment, pages 155-156 (1982).

P. Debye, A.M. Bueche, "Scattering by an Inhomogeneous Solid", J. Appl. Phys. 20, 518-525 (1949).

B. Hammouda, "A New Guinier-Porod Model", J. Appl. Cryst. 43, 716-719 (2010).

G Yuan, X. Wang, D. Wu and B. Hammouda, "Structural Analysis of Dendrimers Based on Polyhedral Oligomeric Silsesquioxane and their Self-Assembly in Solution by Small-Angle Neutron Scattering: Fits to a Modified Two Correlation Lengths Model", Polymer (to be published, 2016).

QUESTIONS

1. What are the three main methods used to analyze SANS data?
2. What is referred to as the Ornstein Zernike functional form? What parameter can be obtained from a fit to that form?
3. What is the meaning of a peak in SANS data (at Q_0 for example)?
4. What type of scattering does the Teubner-Strey model apply to?
5. What are the main parameters for the Guinier-Porod model for elongated scattering objects?

ANSWERS

1. The three main ways used to analyze SANS data are: (1) standard plots (linear plots of functions of I(Q) *vs* functions of Q), (2) non-linear least squares fits to reasonable models

including empirical models and (3) molecularly realistic complex methods for particle shape reconstruction and molecular simulation.
2. The Ornstein-Zernike functional form is a Lorentzian. A correlation length can be obtained.
3. A peak in SANS data (at Q_0) means that there is a structure with a characteristic repeat distance $d = 2\pi/Q_0$.
4. The Teubner-Strey model applies to scattering data with a peak and that decay as $1/Q^4$ at high Q. These are concentrated systems with inter-particle separation distance comparable to particle size or to bicontinuous structures.
5. Data fitting to the Guinier-Porod model yields an intercept G, a radius of gyration R_g, a Porod exponent m and a dimensionality factor for elongated scattering objects 3-s. s=0 for spherical symmetry, s=1 for rods and s=2 for lamellae.